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(54) **Process for preparing an elastomeric copolymer composition of mono-vinyl aromatic hydrocarbons and conjugated dienes**

Verfahren zur Herstellung einer elastomeren Copolymerzusammensetzung aus monovinylaromatischen Kohlenwasserstoffen und konjugierten Dienen

Procédé de préparation d'une composition copolymère élastomère d'hydrocarbures aromatiques mono-vinylés et de diènes conjugués

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**US-A- 4 172 862**

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## Description

**[0001]** The present invention relates to a process for preparing an elastomeric copolymer composition of mono-vinyl aromatic hydrocarbons and conjugated dienes, and to the elastomeric copolymers produced thereby. The elastomeric copolymer according to the present invention possesses the characteristics of enhancing elongatibility ultimately up to 900%, keeping tensile strength within a suitable range and enhancing transparency and adhesive properties.

**[0002]** Di-blocked linear or star-type copolymers of mono-vinyl aromatic hydrocarbon and conjugated diene are well-known and widely used as shoe sole or modified rubber. However, the known material of this type has the drawbacks of inferior transparency and adhesion.

**[0003]** The block copolymer containing conjugated dienes and vinyl aromatic hydrocarbon possesses different properties from those of conventional vulcanization rubbers. The block copolymer possesses comparable physical strength and resilience to that of the vulcanized elastomer under ambient temperature without the aid of vulcanization by curing agents, vulcanizing accelerators or other vulcanizing auxiliaries because of the physical crosslinkage. Additionally, the block copolymer has excellent processability at an elevated temperature similar to a thermoplastic material, thus, it can be processed by injection, extrusion or compression molding processes. Further, the block copolymer can be formulated into various formulations by incorporating suitable thermoplastic resins, such as polystyrene and polyethylene, a softening agent, such as naphthenic oils, and inorganic fillers, such as clay and calcium carbonate, which can be used in the fields of manufacturing shoes or other rubber products, such as toys, window frames, containers, tubing, binders and other modified plastics.

**[0004]** In the manufacturing of an adhesive tape or label, the binder is usually first dissolved in a solvent, then rolled on or sprayed on a substrate. However, this process has numerous drawbacks, such as that the solvent will pollute our environment, and is liable to catch fire, thus, creating an unfavorable working condition. In order to overcome these problems, it is preferable to use a solvent-free binder instead of a solvent-containing binder. Since block copolymers possess excellent balance in adhesion and cohesion, they are a good constituent for forming a binder used in the manufacturing of an adhesive tape or label. United States patent No. 3,427,269 discloses a binder substantially formed from polystyrene-polybutadiene-polystyrene copolymer or polystyrene-polyisoprene-polystyrene copolymer. However, polystyrene-polybutadiene-polystyrene copolymer has the drawbacks of low tackiness and high peel strength. Additionally, the adhesion and other physical properties of the binder will be destroyed if it is substantially formed from polystyrene-polyisoprene-polystyrene copolymer and processed under a high temperature for a long time.

**[0005]** The process according to the present invention can improve the tackiness of the copolymer formed from polystyrene-polybutadiene-polystyrene, and prevent the occurrence of a thermo-degradation phenomenon which is caused by a molecule's shear stress when the copolymer is used under a high temperature for a long time.

**[0006]** United States patent No. 3,251,905 discloses the use of di-lithium initiator to initiate the polymerization of mono-vinyl aromatic hydrocarbons and conjugated dienes, wherein mono-vinyl aromatic hydrocarbons are added when the conjugated dienes are reacted completely; thus, a copolymer in an A-B-A type can be obtained, wherein the mono-vinyl aromatic hydrocarbon monomer is bonded to the end of the conjugated dienes. However, the di-lithium initiator used in this patent has numerous drawbacks, such as the high cost, the poor stability, the complicated syntheses and the low dissolution in general hydrocarbon solvents. Thus, the physical properties of the thermoplastic rubber produced by a di-lithium initiator are unstable. In order to overcome these problems, the di-lithium initiator must be used in high purity and a great amount of polar organic solvent must be used so as to produce a polymer with stable physical properties. Therefore, in addition to the difficulty of purifying the polymer produced by the '905 process, its elastomeric properties are also inferior due to the amount of the vinyl group generated in the polymer structure.

**[0007]** The term "the amount of vinyl group" used in the text refers to the percent by weight of the total amount of the vinyl group when the copolymerized conjugated dienes are polymerized at position 1,2- or 3,4-. For example, if the conjugated diene is 1,3-butadiene, the amount of vinyl group refers to the group at position 1,2-, if the conjugated diene is isoprene, the amount of vinyl group refers to the total amounts of the vinyl groups at positions 1,2- and 3,4-.

**[0008]** U.S. patent No. 3,231,635 discloses a polymerization process whereas mono-vinyl aromatic hydrocarbons are firstly polymerized with a mono-lithium initiator, then conjugated dienes are added, and at last, mono-vinyl aromatic hydrocarbon are added again. This process can produce a thermoplastic elastomer in a type of A-B-A. However, this polymerization process characterized by the addition of all monomers in three steps has the drawback of the existence of impurities which will inactivate the polymerization reaction, and make the transparency inferior. Additionally, the polymerization reaction of the mono-vinyl aromatic hydrocarbon added at the third step has difficult in reacting completely, thus, it is difficult to obtain a product with a homogeneous structure and stable features.

**[0009]** As to the current process of preparing a block copolymer of mono-vinyl aromatic hydrocarbons with conjugated dienes, the mono-vinyl aromatic hydrocarbons are first initiated and polymerized with an organic mono-lithium initiator, the conjugated dienes are then added, and a coupling agent is added at last to proceed with a coupling reaction. This process can prepare a thermoplastic elastomer in (A-B)<sub>n</sub> type. When n=2, the number of the functional groups of the coupling agent is 2, the elastomer is in a linear structure. When n=4, the number of the functional groups of the coupling

agent is 4, the elastomer is in a star-like structure. When  $n \geq 4$ , the elastomer is in a radiative structure. This process is well known for those who are skilled in the art, for example, USP-3,393,182 discloses tin tetrachloride as a coupling agent, USP-3,281,383 discloses silicon tetra-chloride as a coupling agent, USP-3,594,452 discloses hexandyl adipate as a coupling agent, USP-328,183 discloses epoxidized vegetable oil as a coupling agent and USP-3,766,301 discloses phenyl benzoate as a coupling agent. However, this process disclosed in these patents has the following drawbacks:

1. Tin tetrachloride or silicon tetrachloride easily produces a residual chloride salt which corrodes the manufacturing instruments and equipment.

2. When a chlorine-free compound is used as a coupling agent, the impurities formed during the coupling reaction, such as alcohol, phenol, etc., increase the difficulty in the subsequent treatment of water, or in the refinement of solvent.

**[0010]** Furthermore, the coupling efficiency will significantly affect the elastic property of the product regardless of what the coupling agent is. Additionally, the residual impurities after the coupling reaction make the product inferior in transparency and elastomeric properties. When the mono-vinyl aromatic hydrocarbon is styrene and the conjugated diene is butadiene, the polymerized block copolymer is not suitable for adhering because of its weak tackiness and high peel strength.

**[0011]** USP-4,600,749 discloses the use of a mono-lithium initiator to polymerize a mixture of a mono-vinyl aromatic hydrocarbon and a conjugated diene. After the polymerization is complete, further mixture of a mono-vinyl aromatic hydrocarbon and a conjugated diene is added to continuously proceed with further polymerization reaction. This process can produce a thermoplastic block elastomer in a type of B-A-B-A. However, the reaction rate of this process is very slow without the addition a polar solvent, and the amount of mono-vinyl aromatic hydrocarbon polymerized at the first step must be substantially equal to the amount of mono-vinyl aromatic hydrocarbon polymerized at the second step. Thus, this process is not easy to control, and the features of the product are unpredictable, such as the hardness, etc.

**[0012]** In view of the foregoing conventional processes, there are numerous drawbacks which have yet to be overcome, such as:

- the initiator is unstable;
- the polymerization process is too complex;
- the efficiency of coupling reaction is low; and
- the reaction rate is low.

Furthermore, the SBS type copolymer produced by conventional processes would have the so-called necking phenomenon which reduces the elastic resilience. Additionally, these processes can only provide a polymer with a restricted structure other than a broad spectrum of polymeric structures.

**[0013]** The present invention provides an effective process for preparing a block thermoplastic elastomer substantially based on mono-vinyl aromatic hydrocarbons and conjugated dienes with the use of a mono-lithium initiator. The elastomer produced by the instant process has better elastomeric properties than those produced by conventional processes, and has no necking phenomenon. Additionally, the present elastomer possesses better tack co-efficient, thus it is suitable to be used as a glue for an adhesive tape and/or label.

**[0014]** The present invention also provides a novel process for forming two polymers with different polymeric structures. Thus, it is not necessary to use different reactors to primitively polymerize these polymers with different polymeric structures, nor to then blend and polymerize these polymers in a reactor.

**[0015]** The polymers produced by the present process have the features that:

- the ultimate elongation is up to 900%;
- the tensile strength is in a range of 100 to 200 kg/cm<sup>2</sup>;
- the 300% modulus is below 35 kg/cm<sup>2</sup>; and
- the product can be used in the field of adhesives, and possesses excellent transparency, thus, it can be used for producing transparent shoe soles.

**[0016]** The novel process according to the present invention for preparing a mixture combining different block copolymers, comprises two steps:

- 1) under inert atmosphere and in a polar solvent-containing hydrocarbon organic solvent, subjecting mono-vinyl aromatic hydrocarbon monomer (A1), hydrocarbon solvents and polar ether compounds into a reactor, then adding a mono-lithium initiator (II) to initiate a polymerization reaction;

2) when the conversion of the mono-vinyl aromatic hydrocarbon monomer (A1) reaches 99.9%, a mixture of a mono-vinyl aromatic hydrocarbon monomer (A2) and a conjugated diene monomer (B) is immediately added to the same reactor, and further mono-lithium initiator (I2) is added within 4 hours from the addition of the mixture to obtain a mixture having different polymeric structures.

The amount of said mono-vinyl aromatic hydrocarbon monomer (A1 + A2) is 15-90% by weight of the total weight of all the monomers.

[0017] The weight ratio between the initiator (I1) used at 1) step and the initiator (I2) used at 2) step is in a ratio of 50:1 to 1:1, and the weight ratio of A<sub>1</sub>/A<sub>2</sub> is 5/1 to 1/5:

[0018] The conjugated diene monomer (B) used in the present invention has 4 to 6 carbon atoms. Examples of the conjugated diene monomer (B) are 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene and 1,3-pentadiene. The preferred conjugated diene monomer is 1,3-butadiene or isoprene. These dienes can be used separately, or be used as a mixture comprising two or more dienes.

[0019] The mono-vinyl aromatic hydrocarbons (A1 and A2) according to the present invention comprise only one vinyl group. Examples of the mono-vinyl aromatic hydrocarbons (A1 and A2) are styrene, p-methylstyrene, m-methylstyrene, o-methylstyrene, p-ethylstyrene, m-ethylstyrene, o-ethylstyrene,  $\alpha$ -vinyl naphthene,  $\beta$ -vinyl naphthene and  $\alpha$ -methylstyrene. The preferred mono-vinyl aromatic hydrocarbon is styrene. They can be used separately, or be used as a mixture comprising two or more mono-vinyl aromatic hydrocarbons.

[0020] The organic hydrocarbon solvent according to the present invention is just a medium for polymerizing reaction. Examples of the organic hydrocarbon solvent are aliphatic type solvents, such as pentane, hexane, heptane, octane and decane, cycloalkanes, such as cyclopentane, cyclohexane, methylcyclohexane, ethylcyclohexane and 1,4-dimethylcyclohexane, and aromatic hydrocarbon solvents, such as benzene, toluene, ethylbenzene, xylene, diethylbenzene and propylbenzene. These organic hydrocarbon solvents can be used separately, or be used as a mixture comprising two or more organic hydrocarbon solvents.

[0021] Generally, the addition of polar hydrocarbon solvents can reduce the difference in reactivities between the mono-vinyl aromatic hydrocarbon and conjugated diene, and promote the polymerization rate thereof. However, if too much of the polar hydrocarbon solvents is added, the arrangement of the mono-vinyl aromatic hydrocarbon monomer and the conjugated diene monomer in the block copolymer will be confounded, that is, the polymeric structure of the obtained copolymer will be changed from a block structure to a random structure. Thus, the amount range of the polar hydrocarbon solvent which can be used is determined based on the total amounts of the mono-vinyl aromatic hydrocarbon monomer and the conjugated diene monomer, so as to ensure the polymeric structure of the obtained copolymer is a block structure. Examples of the polar hydrocarbon solvent according to the present invention are ethers, such as tetrahydrofuran, furan, diethyl ether, dipropyl ether, cyclic pentyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, diglycol dimethyl ether, preferably tetrahydrofuran and tertiary amines, such as trimethyl amine, triethyl amine and tripropyl amine, preferably triethyl amine.

[0022] The mono-lithium initiator according to the present invention comprises metal lithium or organic lithium compounds of alkyl, cycloalkyl or aromatic hydrocarbyl, such as methyl lithium, ethyl lithium, propyl lithium, butyl lithium, phenyllithium, hexyllithium, 2-ethylhexyllithium, cyclohexyllithium, benzyllithium, ethylphenyllithium and xylyllithium. Among these initiators, it is preferred to use n-butyllithium or sec-butyllithium.

[0023] During the process of preparing a mixture with different block copolymers, the polymerizing system must be kept in a status of being impurity-free. Examples of the impurities are water, oxygen, carbon dioxide, alkynyls, halogens, alkanols, organic acids or inorganic acids. The mono-vinyl aromatic hydrocarbons and conjugated dienes must also be purified before polymerization reaction, and the purifying process must also be carried under nitrogen, argon or helium atmosphere.

[0024] The amount of the mono-vinyl aromatic hydrocarbon monomer used in steps 1) and 2) is 15-90% by weight of the total weight of all the monomers. When the amount is greater than 90 wt%, the elastomeric properties of the product will reduce dramatically and show more plastic-like features. Additionally, precipitates are easily formed during the polymerization process, which make the reaction solution unclear, thus inducing the monomers to be not able to polymerize homogeneously. When the amount is less than 15 wt%, the physical properties (especially elasticity) of the product are significantly destroyed, tensile strength thereof reduces and thermal degradation occurs easily.

[0025] The preferred temperature range of proceeding with the polymerization reaction is -30°C to 150°C, more preferably 30°C to 100°C. If the temperature is too high, the active lithium end of the organic lithium initiator will be inactivated, then, the polymerization reaction is terminated. Further, the possibility of impurities being reacted with active lithium end of the organic lithium initiator increases.

[0026] The weight ratio of organic lithium initiator (I1) to organic lithium initiator (I2) is about 1 to 50. When the ratio is less than 1, the obtained product do not possess the features of an elastomer, and has low hardness and low tensile strength. When the ratio is more than 50, the obtained product is a triblock copolymer, thus its transparency becomes inferior and its ultimate elongation rate cannot reach 900%. Additionally, the tackiness or quick stick is low when for-

mulated as an adhesive in the primitive stage.

[0027] The organic lithium initiator (I2) of step 2) should be added at the time that the mono-vinyl aromatic hydrocarbons and the dienes are added and react with one another, or are added within 4 hours after the beginning of the polymerization reaction. If the organic lithium initiator (I2) of step 2) is added later than 4 hours after the beginning of the polymerization, the product yield becomes very low, and, thus is uneconomical. Furthermore, the amount of the second polymer is too low if the organic lithium initiator (I2) of step 2) is added later than 4 hours after the beginning of the polymerization, thus the desired block copolymer according to the present invention cannot be achieved. Additionally, the delay of the addition of the organic lithium initiator (I2) into the reactor will cause the too-low molecular weight polymer to occur. As a result, the polymer will adhere to inner wall of the reactor, or plug the tubes connected to the reactor as stripping. Generally, the organic lithium initiator (I2) is added during a process lasting for 1 minute to 2 hours.

[0028] The weight amount ratio of the mono-vinyl aromatic hydrocarbon (A1) to the mono-vinyl aromatic hydrocarbon (A2) is 5 to 0.2. When the ratio is higher than 5 or less than 0.2, the heat resistance of the obtained copolymer will be inferior and its hardness or elastomeric properties dramatically reduce.

[0029] The desired copolymer according to the present invention is a product of combining the polymers with different structures. In the product, the polymer with a higher molecular weight is 40-99% of the total polymers, preferably, 60-99%. If the amount of the polymer with a higher molecular weight is less than 40%, the tensile strength of the final copolymer is too low to be used in practice. If the amount is higher than 99%, the structure of the obtained copolymer is similar to those well-known block copolymers, such as SBS, thus, making the transparency and resilience of the product inferior. Also, the necking phenomenon cannot be avoided.

[0030] According to the present invention, there is at least one stabilizer added after the polymerization reaction so as to protect the polymer against the degradation caused by oxygen, UV radiation, ozone and/or heat. After polymerization, the materials such as water, alkanols, organic acids, inorganic acids and phenols which can react with the active lithium end of the organic lithium initiator could be first added. Or, alternatively, after the final product inactivated, the stabilizer is then added. Alternatively, the stabilizer can be directly added into the reactor to act as a terminator. After the polymerization reaction has been terminated, the final solution and/or suspension is coagulated to particles by using hot water. Finally, the product is finished by vaporizing, drying, filtrating and/or centrifuging.

[0031] The number average molecular weight of the present product is  $5 \times 10^3$  to  $50 \times 10^4$ . If the molecular weight is less than  $5 \times 10^3$ , the mechanical properties, such as tensile strength, would be inferior. If the molecular weight is more than  $50 \times 10^4$ , the product is unsuitable for processing. In order to achieve the preferred features, the number average molecular weight is preferably  $3.5 \times 10^4$  to  $35 \times 10^4$ .

#### Examples:

[0032] The present invention will be described in further detail with reference to the following examples.

#### Example 1

[0033] In a 100-liter pressured autoclave equipped with a stirrer and a jacket, 68.8 liters of cyclohexane, 1.4 liters of styrene, and 2 grams of tetrahydrofuran are added. The content in the reactor is heated, and 226 ml of n-butyllithium solution is added when the temperature reaches 62°C. After the conversion of the monomers exceeds 99.9%, a mixture of 6.5 liters of butadiene and 1.7 liters of styrene, and 53 ml of n-butyllithium solution are added to proceed with a second step of polymerization. After the conversion of all the monomers exceeds 99.9%, 0.8 PHR antioxidant (TNPP/Irganox 1076 = 13/7) is added. PHR means the amount/grams chemicals added per 100 grams of rubber.

[0034] The reacting solution possesses two polymers with different polymeric structures due to the addition of the initiator added at step 2). These two polymers are easily miscible. The solid polymers can be recovered from the reaction solution by stripping.

#### Comparative Example 1

[0035] In a 100-liter pressured autoclave equipped with a stirrer and a jacket, 73.8 liters of cyclohexane, 1.8 liters of styrene and 8 grams of tetrahydrofuran are added. The content of the reactor is heated, and 112 ml of n-butyllithium solution is added when the temperature reaches 47°C. After the conversion of the monomers exceeds over 99.9%, 7.3 liters of butadiene is added to proceed with the second stage of polymerization reaction. After the conversion exceeds 99.9%, 1.8 liters of styrene is added to continuously polymerize. When the conversion of the monomers reaches 99.9%, 0.8 PHR antioxidant (TNPP/Irganox 1076=13/7) is added to terminate the activity of the lithium end of the organic lithium initiator. The obtained polymer solution is in a straight block S-B-S type. The solid polymers can be recovered from the reaction solution by stripping.

**Comparative Example 2**

[0036] In a 100-liter pressured autoclave equipped with a stirrer and a jacket, 68.8 liters of cyclohexane, 1.5 liters of styrene are added. When the reactor is heated to 62°C, 270 ml of n-butyl-lithium is added. After the conversion of the monomers has reached 99.9%, 6.35 liters of butadiene and 1.5 liters of styrene are added to the continuously polymerizing reaction. After the conversion of the monomers has reached 99.9%, 0.8 PHR of antioxidant (TNPP/Irganox 1076 =13/7) is added to terminate the active lithium end of the organic lithium initiator. The obtained polymer solution is in a straight block S-B-S type. The solid polymers can be recovered from the reaction solution by stripping

**Results:**

[0037]

Table 1

	Example 1	Comparative Example 1	Comparative Example 2
300% modulus (kg/cm <sup>2</sup> )	29	40	25
Elongation (%)	1100	710	920
Tensile strength (kg/cm <sup>2</sup> )	106	209	105
Transparency (UV 550nm) %	80.0	66.2	70
Hardness (Shore A)	87	87	87
Bound styrene (%)	41.8	41.1	42.6
Melting index (180°C, 5kg, g/10 min)	6.7	5.6	3.5

[0038] As can be seen from Table 1, it is apparent that the product of example 1 is more transparent than those of comparative examples. Additionally, the instant copolymer is suitable for processing, and its elongation rate exceeds 1000%. Thus, it can be used in the field of manufacturing adhesive and the transparent shoe soles.

**Claims**

1. A process for preparing a mixture of different block copolymers, comprising the following two steps of:

1) subjecting mono-vinyl aromatic hydrocarbon monomer (A1), hydrocarbon solvents and ether polar compounds into a reactor, wherein the polar ether compounds are selected from the group comprising tetrahydrofuran, furan, diethyl ether, dipropyl ether, cyclic pentyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol dibutyl ether, diglycol dimethyl ether, then adding a mono-lithium initiator to initiate reaction;

2) as the conversion of the mono-vinyl aromatic hydrocarbon monomer (A1) reaches 99.9%, a mixture of further mono-vinyl aromatic hydrocarbon monomer (A2) and conjugated diene monomer (B) is immediately added to the same reactor, and further mono-lithium initiator is added within 4 hours to obtain a mixture having different polymeric structures,

wherein the number average molecular weight of the mixture is in the range of 5,000 to 500,000, and the amount of said mono-vinyl aromatic hydrocarbon monomer (A1+A2) is 15-90% by weight of the total weight of all the monomers,

**characterized in that:**

the initiator of step 2) is added in the time range of 1 minute to 2 hours, and the initiators at step 1) and step 2) are added in the weight ratio of 1 to 50, and the initiator at step 2) is added within 4 hours after the addition of mono-vinyl aromatic hydrocarbon and conjugated diene; the weight ratio of the mono-vinyl aromatic hydrocarbon (A1) of step 1 to the mono-vinyl aromatic hydrocarbon (A2) of step 2 is 5 to 0.2; and the polymer with a higher molecular weight is present in amount of 40-99%, based on the total polymers.

2. The process as claimed in claim 1, wherein the mono-vinyl aromatic hydrocarbon is styrene, diene.

3. The process as claimed in claim 2, wherein the conjugated diene is 1,3-butadiene, isoprene, and mixture thereof.

4. The process as claimed in claim 1, wherein the process is carried out in the temperature range of 10-120°C, and

in the time range of 30 minutes to 6 hours.

- 5 5. The process as claimed in claim 1, wherein the mono-lithium initiator is selected from the group comprising methyl lithium, ethyl lithium, n-butyl lithium, sec-butyl lithium, tert-butyl lithium, pentyl lithium, phenyl lithium and cyclohexyl lithium.
6. The process as claimed in claim 1, wherein the hydrocarbon is selected from one or two of the following compounds: butane, pentane, n-hexane, cyclohexane, heptane, octane and ethylhexane.
- 10 7. The process as claimed in claim 1, wherein the amount ratio between the mono-vinyl aromatic hydrocarbon monomer of step 1) and the mono-vinyl aromatic hydrocarbon monomer of step 2) is in the range of 0.01 to 100.
8. The process as claimed in claim 1, wherein the total added amount of the initiator is 0.01% to 0.50%, based on the total weight of all monomers.

#### Patentansprüche

- 20 1. Verfahren zur Herstellung einer Mischung von verschiedenen Block-Copolymeren, das die folgenden zwei Verfahrensschritte aufweist:

1) ein monovinylaromatischen Kohlenwasserstoff-Monomer (A1), Kohlenwasserstofflösungsmittel und polaren Etherverbindungen werden in einen Reaktor eingebracht, wobei die polaren Etherverbindungen aus einer Gruppe ausgewählt sind, die Tetrahydrofuran, Furan, Diethylether, Dipropylether, cyclisches Pentylether, Ethylenglycoldimethylether, Ethylenglycoldiethylether, Ethylenglycoldibutylether, Diglycoldimethylether aufweist, und nachfolgend wird ein Mono-Lithiumaktivator hinzugefügt, um die Reaktion zu starten,

2) wenn die Umwandlung des monovinylaromatischen Kohlenwasserstoff-Monomers (A1) 99,9% erreicht, wird eine Mischung mit zusätzlichem monovinylaromatischen Kohlenwasserstoff-Monomer (A2) und konjugierten Dienmonomer (B) sofort dem selben Reaktor und zusätzlicher Mono-Lithiumaktivator innerhalb von 4 Stunden hinzugefügt, um eine Mischung mit unterschiedlichen Polymerstrukturen zu erhalten, wobei die Zahl des mittleren Molekulargewichts der Mischung in dem Bereich von 5.000 bis 500.000 liegt und der Anteil des monovinylaromatischen Kohlenwasserstoff-Monomers (A1+A2) 15-90 Gew.-% des Gesamtgewichts aller Monomere beträgt,

**dadurch gekennzeichnet, daß**

der Aktivator aus Schritt 2 in einem Zeitraum von 1 Minute bis 2 Stunden zugesetzt wird und der Aktivator aus Schritt 1 und 2 in einem Gewichtsverhältnis von 1:50 zugesetzt werden und der Aktivator aus Schritt 2 innerhalb von 4 Stunden nach der Hinzugabe des monovinylaromatischen Kohlenwasserstoffs und des konjugierten Dien hinzugesetzt wird, wobei der monovinylaromatische Kohlenwasserstoff (A1) aus Schritt 1 zu dem monovinylaromatischen Kohlenwasserstoffs (A2) aus Schritt 2 in einem Gewichtsverhältnis von 5-0,2 steht, und das Polymer mit einem höheren Molekulargewicht in einer Menge von 40-99 % bezogen auf die gesamten Polymere vorhanden ist.

2. Verfahren nach Anspruch 1, bei dem der monovinylaromatische Kohlenwasserstoff Styren, Dien ist.
- 45 3. Verfahren nach Anspruch 2, bei dem das konjugierte Dien 1,3-Butadien, Isopren und eine Mischung dieser ist.
4. Verfahren nach Anspruch 1, bei dem der Prozeß in einem Temperaturbereich von 10-120°C ausgeführt wird und der Zeitraum zwischen 30 min und 6 Stunden liegt.
- 50 5. Verfahren nach Anspruch 1, bei dem der Mono-Lithiumaktivator aus der Gruppe ausgewählt ist, die Methyllithium, Ethyllithium, N-Butyllithium, Sec-Butyllithium, Tert-Butyllithium, Pentyllithium, Phenyllithium und Cyclohexyllithium aufweist.
- 55 6. Verfahren nach Anspruch 1, bei dem der Kohlenwasserstoff ausgewählt ist aus ein oder zwei der folgenden Verbindungen: Butan, Pentan, N-Hexan, Cyclohexan, Heptan, Octan und Ethylhexan.
7. Prozeß nach Anspruch 1, bei dem das Mengenverhältnis zwischen dem monovinylaromatischen Kohlenwasserstoff-Monomer aus Schritt 1 und dem monovinylaromatischen Kohlenwasserstoff-Monomer aus Schritt 2 ein Ver-

hältnis im Bereich von 0,01-100 vorliegt.

8. Verfahren nach Anspruch 1, bei dem die insgesamt zugesetzte Menge des Starters 0,01% bis 0,50% bezogen auf das Gesamtgewicht aller Monomere ist.

## Revendications

1. Un procédé pour préparer un mélange de copolymères séquencés différents, comprenant les deux étapes suivantes :

1) placer un monomère du type hydrocarbure aromatique monovinyle (A1), des solvants du type hydrocarbure et des éthers polaires dans un réacteur, les éthers polaires étant choisis dans la classe formée par le tétrahydrofuranne, le furanne, l'éther de diéthylique, l'éther de dipropyle, l'éther de pentyle cyclique, l'éther diméthylque d'éthylène-glycol, l'éther diéthylque d'éthylène-glycol, l'éther dibutylque d'éthylène-glycol, l'éther diméthylque de diglycol, puis ajouter un initiateur monolithié pour initier la réaction ;

2) lorsque la conversion du monomère du type hydrocarbure aromatique monovinyle (A1) atteint 99,9 %, ajouter immédiatement un mélange d'un supplément de monomère du type hydrocarbure aromatique monovinyle (A2) et d'un monomère du type diène conjugué (B) dans le même réacteur, et ajouter un supplément d'initiateur monolithié dans les 4 heures pour obtenir un mélange ayant des structures polymères différentes,

le poids moléculaire moyen en nombre du mélange étant compris dans l'intervalle de 5000 à 500 000, et la quantité dudit monomère du type hydrocarbure aromatique monovinyle (A1 + A2) étant de 15 à 90 % en poids du poids total de tous les monomères,

caractérisé en ce que :

l'initiateur de l'étape 2) est ajouté en un intervalle de temps de 1 minute à 2 heures, et les initiateurs de l'étape 1) et de l'étape 2) sont ajoutés en un rapport en poids de 1 à 50, et l'initiateur de l'étape 2) est ajouté dans les 4 heures après l'addition de l'hydrocarbure aromatique monovinyle et du diène conjugué ; le rapport en poids de l'hydrocarbure aromatique monovinyle (A1) de l'étape 1 à l'hydrocarbure aromatique monovinyle (A2) de l'étape 2 est de 5 à 0,2 ; et le polymère ayant un poids moléculaire supérieur est présent en une quantité de 40 à 99 %, par rapport aux polymères totaux.

2. Le procédé tel que revendiqué dans la revendication 1, dans lequel l'hydrocarbure aromatique monovinyle est le styrène, le diène.
3. Le procédé tel que revendiqué dans la revendication 2, dans lequel le diène conjugué est le 1,3-butadiène, l'isoprène ou un mélange d'entre eux.
4. Le procédé tel que revendiqué dans la revendication 1, dans lequel le procédé est exécuté dans un intervalle de température de 10 à 120°C, et dans un intervalle de temps de 30 minutes à 6 heures.
5. Le procédé tel que revendiqué dans la revendication 1, dans lequel l'initiateur monolithié est choisi dans la classe formée par le méthyl-lithium, l'éthyl-lithium, le *n*-butyl-lithium, le *sec*-butyl-lithium, le *tert*-butyl-lithium, le pentyl-lithium, le phényl-lithium et le cyclohexyl-lithium.
6. Le procédé tel que revendiqué dans la revendication 1, dans lequel l'hydrocarbure est choisi parmi un ou deux des composés suivants : butane, pentane, *n*-hexane, cyclohexane, heptane, octane et éthylhexane.
7. Le procédé tel que revendiqué dans la revendication 1, dans lequel le rapport de quantités entre le monomère du type hydrocarbure aromatique monovinyle de l'étape 1) et le monomère du type hydrocarbure aromatique monovinyle de l'étape 2) est compris dans l'intervalle de 0,01 à 100.
8. Le procédé tel que revendiqué dans la revendication 1, dans lequel la quantité ajoutée totale de l'initiateur est de 0,01 % à 0,50 %, par rapport au poids total de tous les monomères.